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EFFECT OF SELECTED PARAMETERS ON PREDICTIONS OF A PHOTOCHEMICAL MODEL

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ABSTRACT

A sensitivity study was undertaken to assess the effect of selected parameters on the predictions of a photochemical kinetics model. The model was previously developed for use in designing control requirements for ozone reduction in urban areas. The parameters that were varied in the present study included (1) solar energy, (2) dilution rate, (3) post-9 A.M. emissions, and (4) hydrocarbon composition of 6-9 A.M. emissions. Based on the results of the simulations for each of these parameters, O_3 isopleths as a function of initial NMHC and NO_x were constructed. A comparison of the degree of hydrocarbon control predicted to achieve the air quality standard for O_3 was made for each set of isopleths. It was found that the predictions of the model are largely insensitive to the parameters investigated when the results of the simulations are interpreted in a relative sense.

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SECTION I

INTRODUCTION

A method (1) was proposed recently for deriving ozone-precursor relationships for use in planning control requirements for urban ozone reduction. The method was based on the combined results of smog chamber data and photochemical modeling techniques. A model was first developed to fit the maximum 1-hour average O_3 levels obtained in smog chamber studies (2,3) of irradiated auto exhaust and oxides of nitrogen (NO_x) mixtures. The model was then adjusted to conditions that more closely approximate those of the polluted atmosphere. This adjusted model was used to construct a series of ozone isopleths over a wide range of initial pollutant levels. A detailed version of these isopleths, for typical urban concentrations of nonmethane hydrocarbon (NMHC) and NO_x, is shown in Figure 1. The chemical kinetics mechanism used to construct this set of isopleths is given in the Appendix.

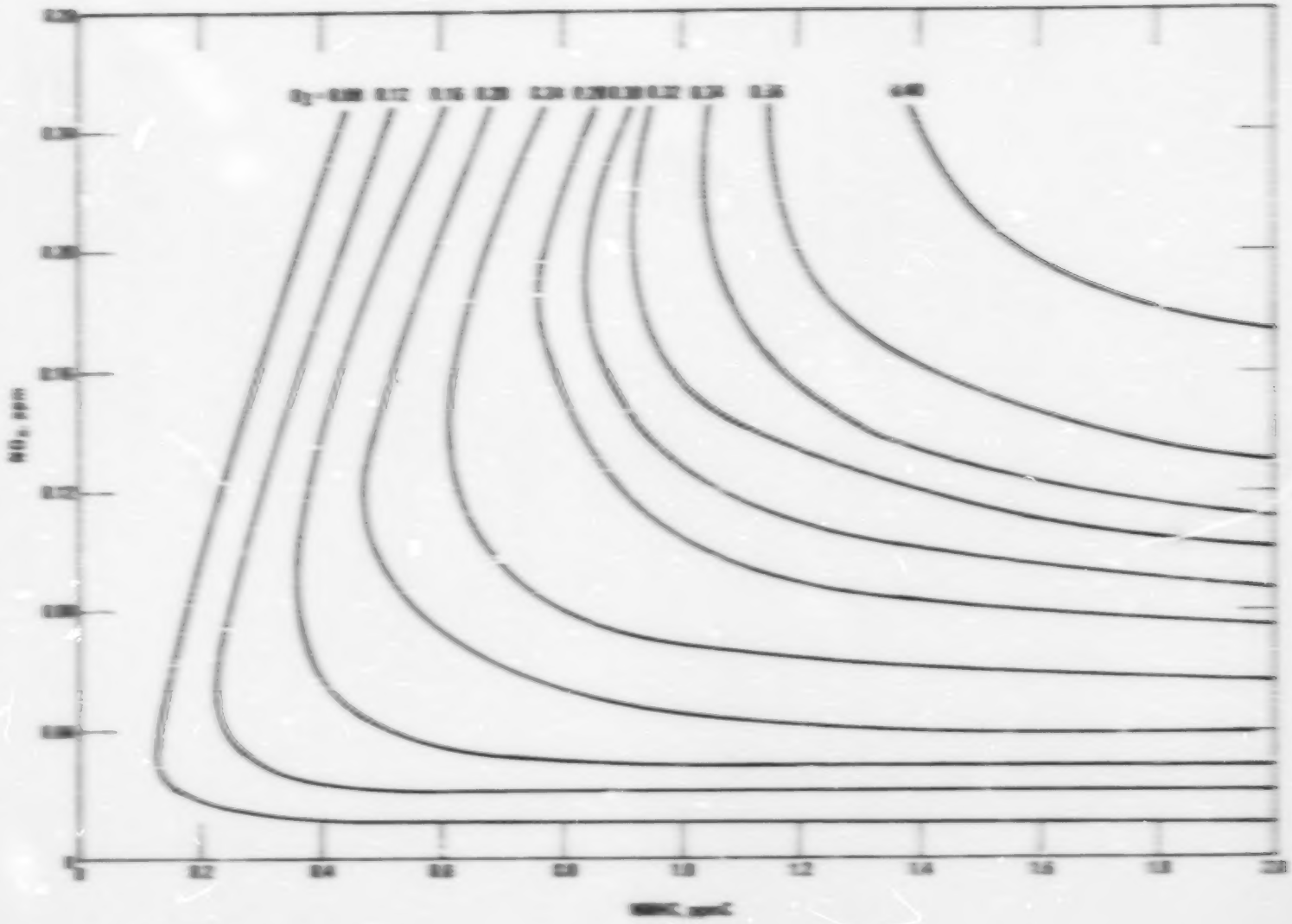
A complete description of the conditions used to generate the isopleths is found elsewhere (1) and only the highlights will be included in this present work. The principal components of the model used to derive the isopleths of Figure 1 are as follows:

(1) The hydrocarbon mix consisted of 25% propylene and 75% n-butane (as carbon). Initial NO_2 levels were taken to be 25% of the initial NO_x concentrations.

(2) Diurnal 1-hour average values of the photolytic rate constants, corresponding to the summer solstice for Los Angeles (34°N latitude), were used.

(3) Simulations were carried out for a 9-hour period corresponding to the hours between 8 A.M. and 5 P.M. (DT (local daylight saving time).

(4) Simulations were begun with a full charge of reactants. There was no addition of fresh emissions in the subsequent 9 hours of the simulations.



(5) A dispersion rate of 3 percent per hour was included in the calculations. A low dispersion rate was chosen to simulate conditions of high stagnation in urban areas where the afternoon mixing height is relatively low. Such conditions are found along the West Coast during the summer months.

The purpose for constructing a set of isopleths was to offer an alternative to the existing Appendix J method (4) for calculating ozone-precursor control requirements. A detailed description of how these isopleths can be used to estimate the degree of reduction in ambient precursor levels needed to attain a specified level of ozone can be found elsewhere (5). It is the intent of this method to offer a single set of isopleths that can be applied to any urban area. The sensitivity study presented here was undertaken in an effort to estimate whether or not the set of isopleths shown in Figure 1 could be applied universally to calculate control requirements. There are a number of limitations arising from the assumptions that were made to derive the ozone isopleths. These assumptions may be too restrictive to allow universal application of the isopleths. Some of the most serious limitations are:

(1) The model was developed to fit chamber data (2,3) of irradiated auto exhaust and NO_x mixtures. The method, therefore, ignores organic emissions from non-exhaust sources. It is known, however, that non-exhaust sources can account for a significant fraction of the organic emissions in urban areas (6,7). The reactivity, therefore, of the hydrocarbon mix used in this modeling exercise may not be comparable to the reactivity of the organic emissions in various control districts throughout the country.

(2) The light intensity selected for this modeling study corresponds to the summer solstice for Los Angeles. This is substantially higher than the insolation prevalent in northern cities. The isopleths, therefore, may not be applicable to northern locations.

(3) A small dilution rate of only 3 percent per hour was used in the simulations to reflect the dispersion of pollutants. Dispersion rates in other areas of the country are significantly greater, and, consequently, the isopleths may not be applicable to these other areas.

(4) The impact of post - 9 A.M. emissions was not considered in the modeling

study. This over-simplification of the real world situation may negate the usefulness of the O_3 isopleths.

To determine how the assumptions cited above affect the predictions of the model, a sensitivity study was undertaken. Results of this sensitivity study can be used to provide insight about the general applicability of the isopleths for estimating the impact of control strategies. In this study selected parameters were varied in order to assess the effect of these parameter on the shape and spacing of the O_3 isopleths. The parameters considered were the following:

light intensity
dilution rate
post - 9 A.M. emissions
hydrocarbon composition of the 6-9 A.M. emissions

In the following section, the results of each of these changes on the predictions of the model are discussed. Also presented is a discussion on how these changes relate to proposed control requirements.

SECTION 2

RESULTS OF SENSITIVITY STUDIES

LIGHT INTENSITY

The isopleths shown in Figure 1 were constructed using photolytic rate constants that correspond to the summer solstice for 34°N latitude (Los Angeles). This is close to the maximum solar intensity occurring in the continental United States. Northeast areas of the country generally experience their worst air pollution episodes in late summer or early fall. The available solar energy at these times and locations is substantially less than the energy available on June 21st in Los Angeles. To assess the impact of a reduction in light intensity, the model was exercised using rate constants for the various photolytic reactions that correspond to September 15th for a 40°N latitude. (Philadelphia is located approximately at this latitude.) At the new location and time, the integrated rate constant for the photodissociation of NO_2 (k_1) over the 9-hour period of the simulations is 20% less than its integrated value for June 21st at 34°N latitude. The peak value of k_1 for the new case is lower by approximately 10%.

The effect of light intensity on the absolute levels of O_3 produced and how these differences in O_3 levels affect predicted control requirements are discussed separately.

Effect on Predicted Maximum O_3 Levels

The effect of decreasing the light intensity on the maximum 1-hour average O_3 concentration is given in Table 1 for selected simulations. The NMHC-to-NO_x ratio was varied from 1.25 to 50. Column (4) in the table lists the maximum 1-hour average O_3 concentrations achieved when photolytic rate constants corresponding to the summer solstice and 34°N latitude were used. Column (5) lists the O_3 values obtained for September 15th at 40°N latitude. Column (6) gives the percent decrease in peak O_3 resulting from the reduced

TABLE 1. EFFECT OF LIGHT INTENSITY ON MAXIMUM 1-HOUR O_3 LEVELS

(1)	(2)	(3)	(4)	(5)	(6)
			Maximum 1-hour ozone		
NMHC/NO_x (ppmC/ppm)	NMHC (ppmC)	NO_x (ppm)	Summer 34°N (ppm)	Fall 40°N (ppm)	% Decrease
1.25	0.25	0.20	0.1670	0.1625	26
1.67	0.25	0.15	0.1856	0.1845	23
2.5	0.25	0.10	0.2104	0.2060	15
3.33	0.50	0.15	0.2396	0.2377	10
5	0.25	0.05	0.2526	0.2518	6
6.67	1.0	0.15	0.2922	0.2905	5
10	2.0	0.20	0.3426	0.3407	4
10	0.5	0.05	0.3170	0.3164	4
12.5	0.25	0.02	0.2098	0.2074	4
20	1.0	0.05	0.2997	0.2955	7
20	2.0	0.10	0.3319	0.3295	7
40	2.0	0.05	0.3224	0.2902	10
50	1.0	0.02	0.1534	0.1524	7

solar intensity. The decrease in O_3 ranges from 23% at the very low NMHC/NO_x ratios to 4% at the higher ratios. The greater decrease at the low NMHC/NO_x ratios is the result of NO inhibition. In this range, the concentration of NO is large relative to the hydrocarbon concentration. Nitric oxide, therefore, is not oxidized until late in the simulation. Because the onset of O_3 formation is delayed, the reduced light intensity leads to a proportionately greater decrease in O_3 concentration than is found for the more reactive NMHC and NO_x systems.

Although the change in O_3 levels varies from 4 to 23% for the simulations cited in Table 1, the change in maximum O_3 varies between only 4 and 7% for NMHC-to-NO_x ratios of 5:1 to 20:1. This is the range of NMHC-to-NO_x ratios that is most commonly encountered in urban areas (5). A decrease in light intensity within this range leads to a proportionate decrease in maximum O_3 levels. A set of isopleths, therefore, generated at the lower light intensity should have the same shape and relative spacing as the set generated at the higher light intensity. If the shape and spacing of two sets of isopleths are identical, the control requirements calculated from the two sets should also be identical. It is shown in the following section that this is the case.

Effect on Predicted Control Requirements

The proposed control method (5) is applied by calculating the percent reduction in ambient precursor levels needed to achieve a specified level of ozone. It is advantageous, therefore, to look at the effect of light intensity in terms of this application rather than to test the sensitivity of the model only in terms of the absolute values predicted for O_3 concentrations. To gauge the effect of varying the light intensity on control requirements, a set of O_3 isopleths was constructed for the reduced solar intensity. The new set is shown in Figure 2. There is little difference in the shape and spacing of these isopleths from the original set shown in Figure 1. This is demonstrated in Figure 3 where the 0.08 and 0.30 ppm O_3 isopleths are shown for the two cases. The solid lines are the isopleths generated at the reduced light intensity. The dashed lines are the corresponding isopleths of Figure 1 generated at the higher light intensity.

The proposed control method for relating ozone to its precursors depends only on the shape and relative spacing of the isopleths and not on the absolute

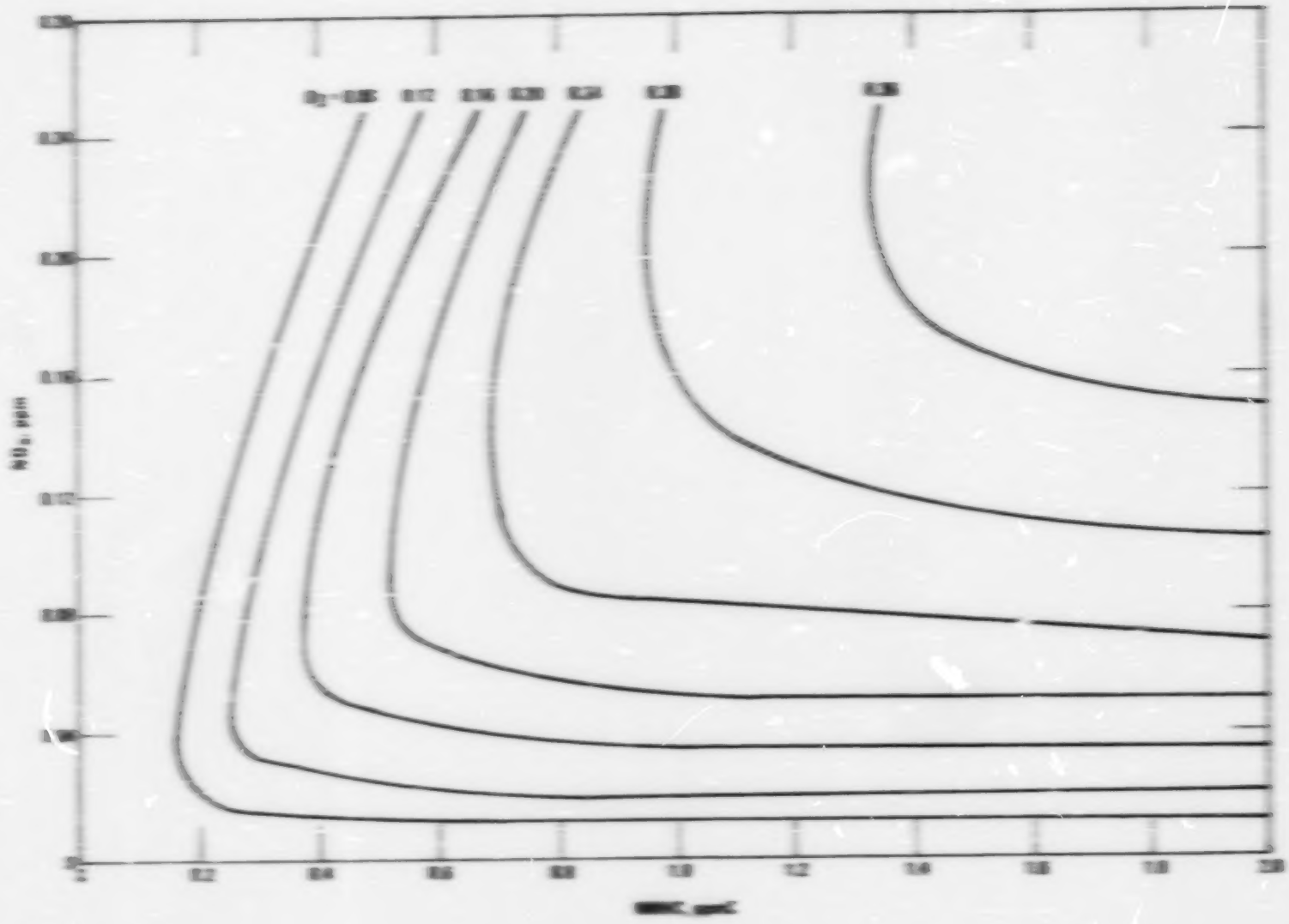


Figure 2. ϕ_3 isopleths for reduced light intensity.

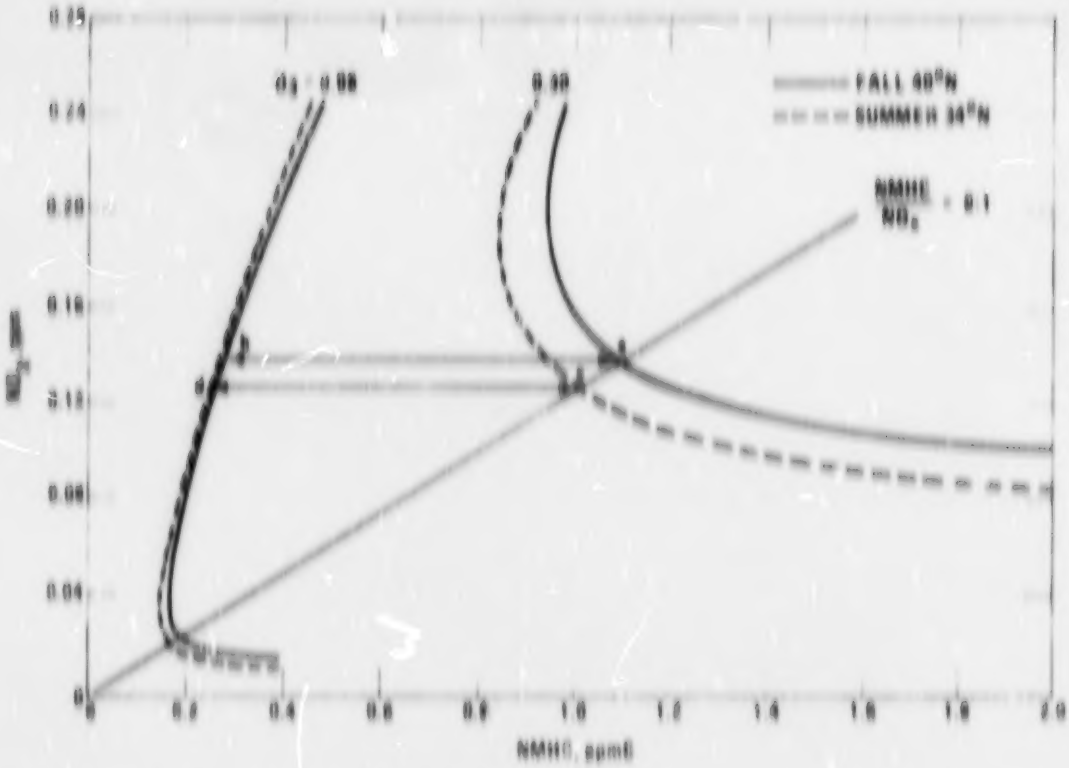


Figure 3. Comparison of isopleths generated at different light intensities.

values of O_3 predicted for given NMHC and NO_x levels. Since the relative spacing and shape of the curves shown in Figures 1 and 2 are little changed, control requirements based on the two sets of isopleths should be nearly the same. The example diagrammed in Figure 3 indicates that this is the case. In this example, the degree of NMHC control needed to reduce ozone from a value of 0.30 ppm to the air quality standard of 0.08 ppm is depicted for a NMHC-to-NO_x ratio of 8:1. At the lower light intensity, to reduce O_3 from 0.30 ppm to 0.08 ppm at constant NO_x, it is necessary to move from point a to point b on the diagram. This corresponds to a decrease in NMHC of from 1.10 to 0.27 ppm. This is a reduction in NMHC of 75%. To meet the standard at the higher light intensity, it is necessary to move from point c to point d. This entails reducing NMHC from 1.01 to 0.25 ppm. This also corresponds to a hydrocarbon reduction of 75%.

Other examples of the percent reduction in NMHC determined from the

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two sets of isopleths are given in Table 2. In this table, the percent reduction in NMHC needed to reduce O_3 from a value of "X" to the standard of 0.08 ppm is shown for typical urban NMHC-to-NO_x ratios ranging from 3:1 to 20:1. Columns (3) and (6) list the NMHC values corresponding to an O_3 concentration of "X" for the high and low solar intensity cases, respectively. Columns (4) and (7) give the NMHC values corresponding to 0.08 ppm ozone for the two cases. The percent reduction in NMHC needed to reduce O_3 concentrations from O_3 = X to O_3 = 0.08 ppm at constant NO_x is given for both cases in columns (5) and (8). Column (9) lists the relative percent change in the amount of NMHC control predicted from the two sets of isopleths. For all of the examples in this table, the relative change in control requirements calculated from the two isopleths varies at most by 5%. On the average, the relative change in needed NMHC control is only 1%, with greater control needed at the higher light intensity. Since this difference is minimal, it can be concluded that predicted control requirements for hydrocarbons are relatively insensitive to variations in light intensity.

DILUTION RATE

The isopleths in Figure 1 were generated using a constant dilution rate of 3 percent per hour throughout the nine-hour simulation period. This low rate of dispersion is reflective of the West Coast area where in summer months there is normally only a 100-meter difference between the mean morning and afternoon mixing heights (8). In other regions of the country, the afternoon mixing height can be substantially greater than the morning mixing height. As an example, in Houston, the mean summer afternoon mixing height is 1500 meters whereas the mean morning mixing height is only 650 meters (8). If uniform lifting of the inversion layer occurs over a 6-hour period, this difference in mixing heights corresponds approximately to a dilution rate of 20 percent per hour.

To assess the effect of dilution rate on the shape and spacing of the isopleths, the simulations used to derive Figure 1 were repeated using a constant dilution rate of 20 percent per hour. The impact of this change on ozone formation and on proposed control requirements is discussed in the following sections.

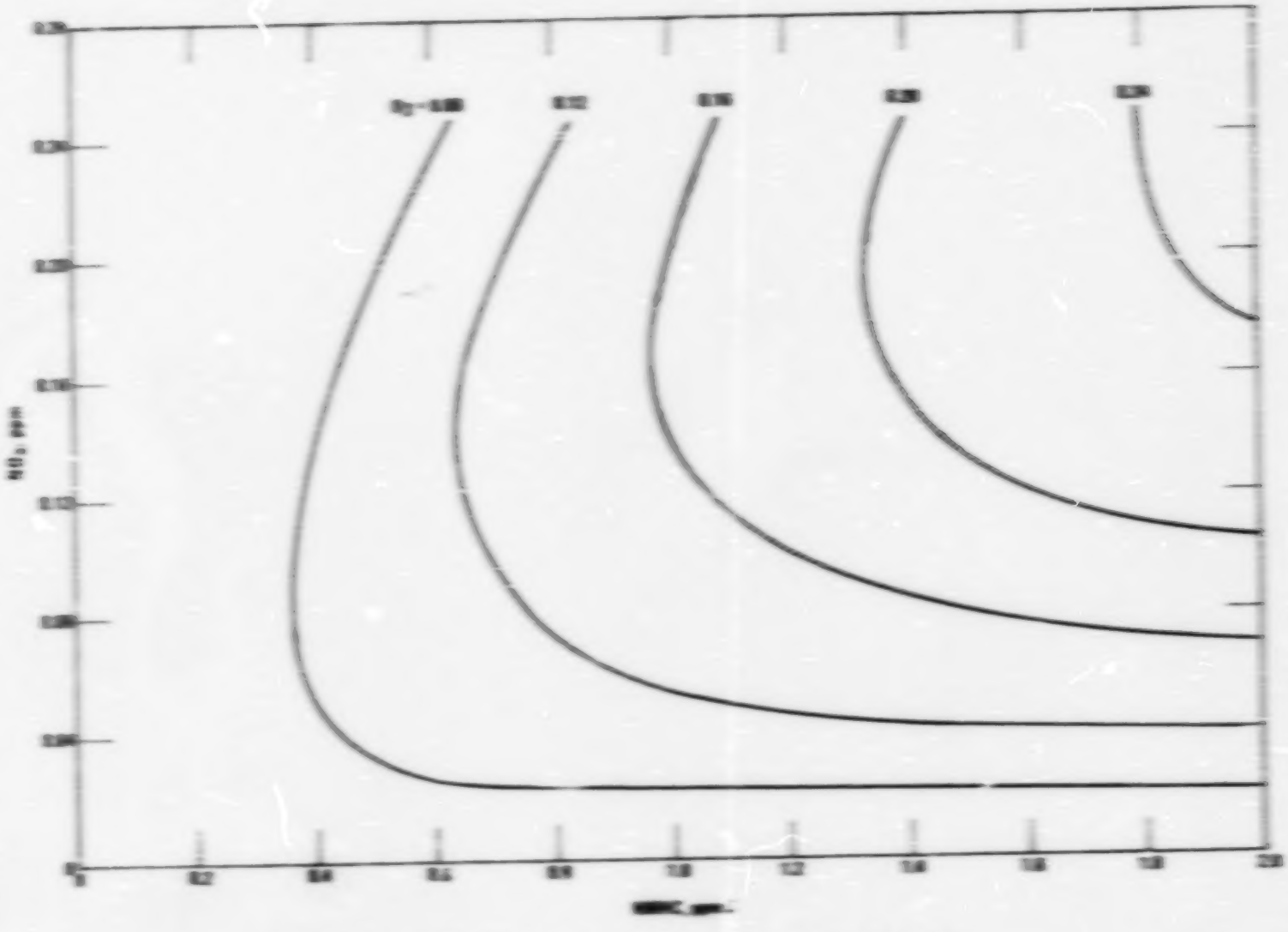

Figure 4. O_3 isopleths for 20 percent per hour dilution.

Effect on Predicted Maximum O_3 Levels

The differences in maximum 1-hour average O_3 concentrations predicted when the dilution rate is increased from 3 to 20 percent per hour are shown in Table 5 for a few simulations selected at random. The percent decrease in O_3 obtained when the dilution rate was increased to 20 percent per hour varied from 30 to 52%, with an average decrease of 45%. The variation seems to be independent of the NMHC-to-NO_x ratio. In general, the smallest decrease in O_3 occurred at the higher hydrocarbon concentrations.

Effect on Predicted Control Requirements

The isopleths generated at the high dilution rate are shown in Figure 4. They can be compared most easily to the original isopleths of Figure 1 by looking at the differences in the 0.08 and 0.20 ppm O_3 isopleths shown in Figure 5. It can be seen that the shape of the two sets of isopleths is approximately the same, but there is a difference in their relative spacing.

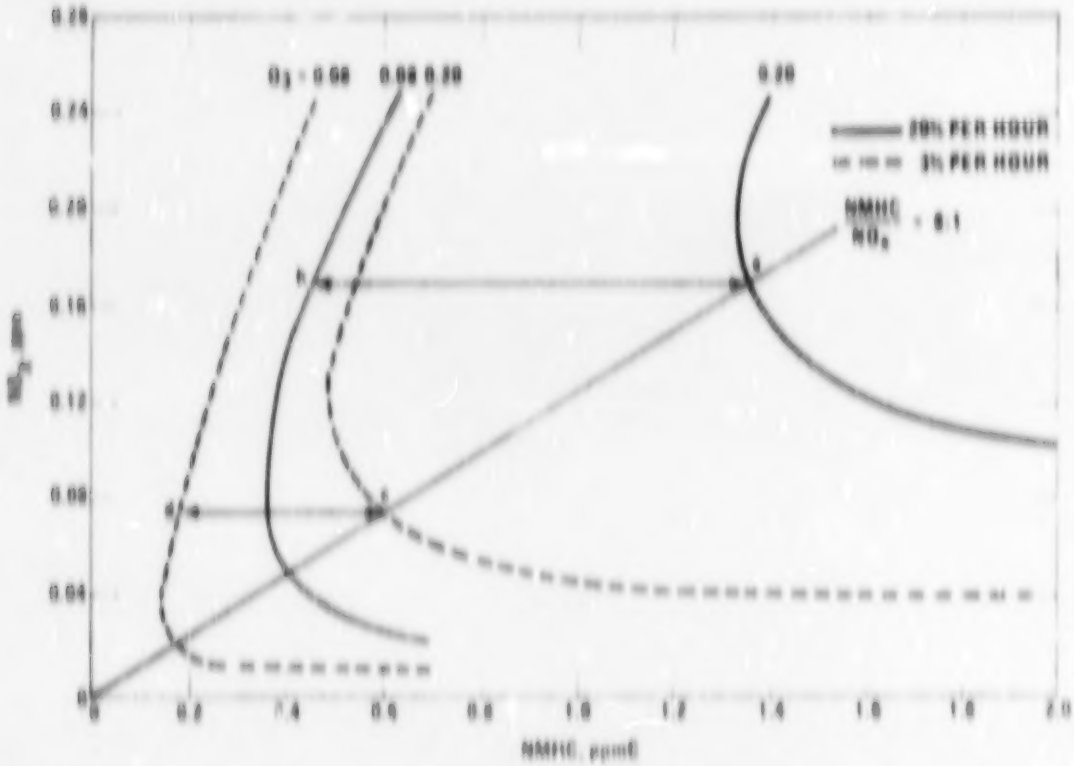

Figure 5. Comparison of isopleths generated for different dilution rates.

TABLE 3. EFFECT OF DILUTION ON MAXIMUM 1-HOUR O_3 LEVELS

[1]	[2]	[3]	[4]	[5]	[6]
			Maximum 1-hour ozone		
VOC/NO_x (ppmC/ppm)	VOC (ppm.)	NO_x (ppm)	3% per hour (ppm)	20% per hour (ppm)	% Decrease
2.5	0.25	0.10	0.194	0.056	46
5	0.25	0.05	0.126	0.060	52
7	0.50	0.10	0.200	0.096	52
5	1.0	0.20	0.332	0.160	52
6.67	1.0	0.15	0.317	0.167	48
10	0.50	0.05	0.170	0.094	45
10	1.0	0.10	0.274	0.146	47
10	2.0	0.20	0.426	0.248	42
12.5	0.25	0.02	0.098	0.049	50
13.33	2.0	0.15	0.386	0.251	35
20	2.0	0.10	0.318	0.195	39
25	0.50	0.02	0.118	0.064	46
40	2.0	0.05	0.224	0.137	39
50	1.0	0.02	0.154	0.076	51
75	1.5	0.02	0.140	0.085	41

An example of how this difference in relative spacing affects control requirements is depicted in Figure 5. At a NMHC-to-NO_x ratio of 8:1 and an O_3 level of 0.20 ppm, to meet the O_3 standard at a dilution rate of 20 percent per hour, the NMHC level should be reduced from 1.36 ppm (point a) to 0.41 ppm (point b) or a predicted reduction of 68%. Similarly, at a dilution rate of 3 percent per hour, the NMHC should be decreased along line cd from 0.59 to 0.18 ppm or a predicted hydrocarbon reduction of 67%. There is, therefore, a difference of only 1% in the degree of hydrocarbon control predicted from these two sets of isopleths. This example and others are summarized in Table 4. The two sets of isopleths predict relative percent changes in NMHC control requirements that vary by only 1 to 5%. On the average there is a 3% relative change in control requirements calculated from the two sets of isopleths. In general, greater control is needed at the lower dilution rate.

POST - 9 A.M. EMISSIONS

The simulations used to generate the O_3 isopleths of Figure 1 were carried out assuming full loading of hydrocarbon and NO_x emissions at 9 A.M. LDT when the simulations were begun. The initial concentrations of NMHC and NO_x used in the modeling runs are intended to represent the mean 6-9 A.M. ambient level of these pollutants. The modeling studies ignore the impact of post - 9 A.M. emissions. In a typical urban area, the vehicular miles driven between 9 A.M. and 4 P.M. can be at least as great as the number of miles driven between 6 and 9 A.M. (9). It is not unreasonable, therefore, to expect a doubling of the early morning emission levels during the 9-hour period of the simulations.

To assess the impact of continuous emissions on the predictions of the model, the simulations used to derive the Figure 1 isopleths were repeated assuming there was a 100% increase in the 6-9 A.M. NMHC and NO_x levels between the hours of 9 A.M. and 5 P.M. LDT. The same initial concentrations of hydrocarbon and NO_x reactants were used to start the simulations at 6 A.M. LDT, but between the hours of 9 A.M. and 5 P.M., NMHC and NO_x emissions, at a constant rate of 12.5 percent per hour, were added to the system. (Fresh emissions were not added between 6 and 9 A.M. because the initial starting reactants are taken to represent the mean 6-9 A.M. levels of NMHC and NO_x.)

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The composition of the added hydrocarbon emissions was the same as the composition of the 6-9 A.M. hydrocarbon mix (i.e. 75% n-butane and 25% propylene). The NO_2 concentration of the added continuous injection was taken to be 10% of the NO_x since almost all oxides of nitrogen are emitted in the form of NO. (The 6-9 A.M. NO_2 concentration, however, was taken to be 25% of the initial NO_x as in the original simulations. This higher NO_2 concentration was used to reflect the presence of aged pollutants in an urban area resulting from carry-over from the preceding day or transport from upwind locations.) The only change, therefore, between these simulations and those used to generate the isopleths of Figure 1 is that there is a doubling of hydrocarbons and NO_x reactants over the nine-hour period.

Effect on Predicted Maximum O_3 Levels

The impact of continuous emissions on the predicted maximum 1-hour average O_3 concentration is shown in Table 5 for selected simulations with HHEC/NO_x ranging from 1.25 to 25. Column (6) lists the percent increase in maximum O_3 that results when continuous emissions are added to the model. The increase ranges from -33% to + 37%. At the low HHEC/NO_x ratio (=2.5:1), there is a decrease in peak O_3 levels when emissions are added throughout the simulation because of the inhibition effect of NO. In this range, NO is already present at a level that is high compared to the hydrocarbon level. The addition of fresh sources of NO tends to suppress O_3 formation. At the higher HHEC-to-NO_x ratios (=2.5:1), the added emissions further drive the system and lead to an increase in O_3. However, even at these higher ratios, the nonlinearity of the smog system is readily apparent. For example, at HHEC-to-NO_x ratios commonly encountered in urban areas (5:1 to 20:1), a 100% increase in reactants results in an increase in O_3 of between only 12 and 37%, with an average increase of 25%.

Effect on Predicted Control Requirements

The O_3 isopleths generated when continuous emissions were included in the model are shown in Figure 6. The shapes of the two sets of curves are comparable, but the relative spacing of the new set of isopleths is somewhat different from the spacing of the isopleths of Figure 1. This is more apparent in Figure 7 where the 0.08 and 0.30 ppm isopleths of Figures 1

TABLE 5. EFFECT OF POST-6 A.M. EMISSIONS ON MAXIMUM 1-HOUR O_3 LEVELS

(1)	(2)	(3)	(4)	(5)	(6)
			Maximum 1-hour ozone		
$NMHC/NO_x$ (ppmC/ppm)	NMHC (ppmC)	NO_x (ppm)	Without Added Emissions (ppm)	With Added Emissions (ppm)	% Increase
1.25	0.25	0.20	0.058	0.039	-33
1.67	0.25	0.15	0.054	0.042	-25
2.5	0.50	0.20	0.152	0.150	- 1
3.33	0.50	0.15	0.195	0.247	26
5	1.0	0.20	0.332	0.412	24
5	0.50	0.10	0.208	0.278	34
5	0.25	0.05	0.126	0.172	37
10	2.0	0.20	0.426	0.495	16
10	1.0	0.10	0.274	0.338	23
12.5	0.25	0.02	0.098	0.129	32
20	2.0	0.10	0.316	0.355	12
20	1.0	0.05	0.207	0.253	22
25	0.50	0.02	0.118	0.152	29

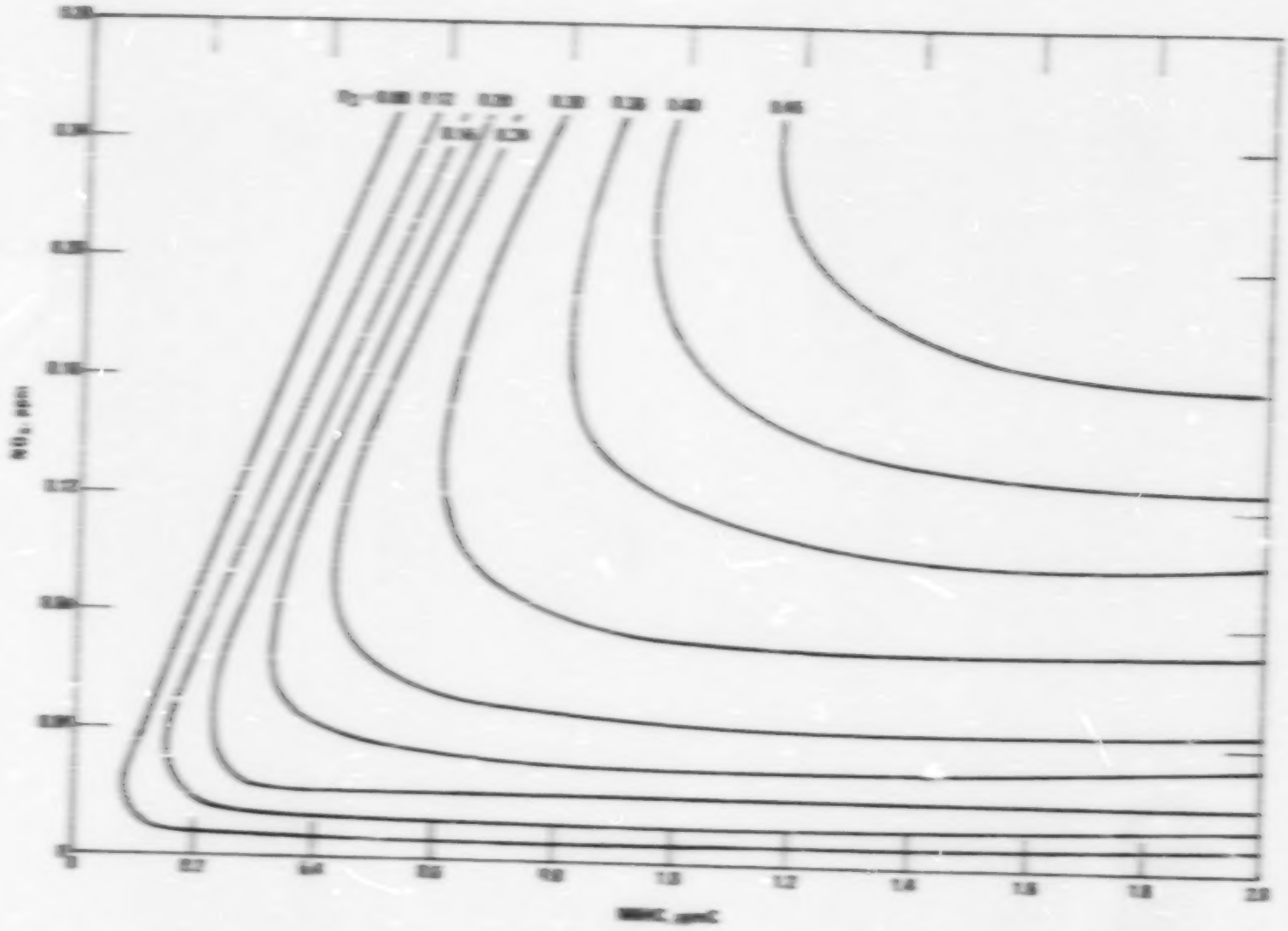

Figure x. O_3 isopleths for post - 9 A.M. emissions.

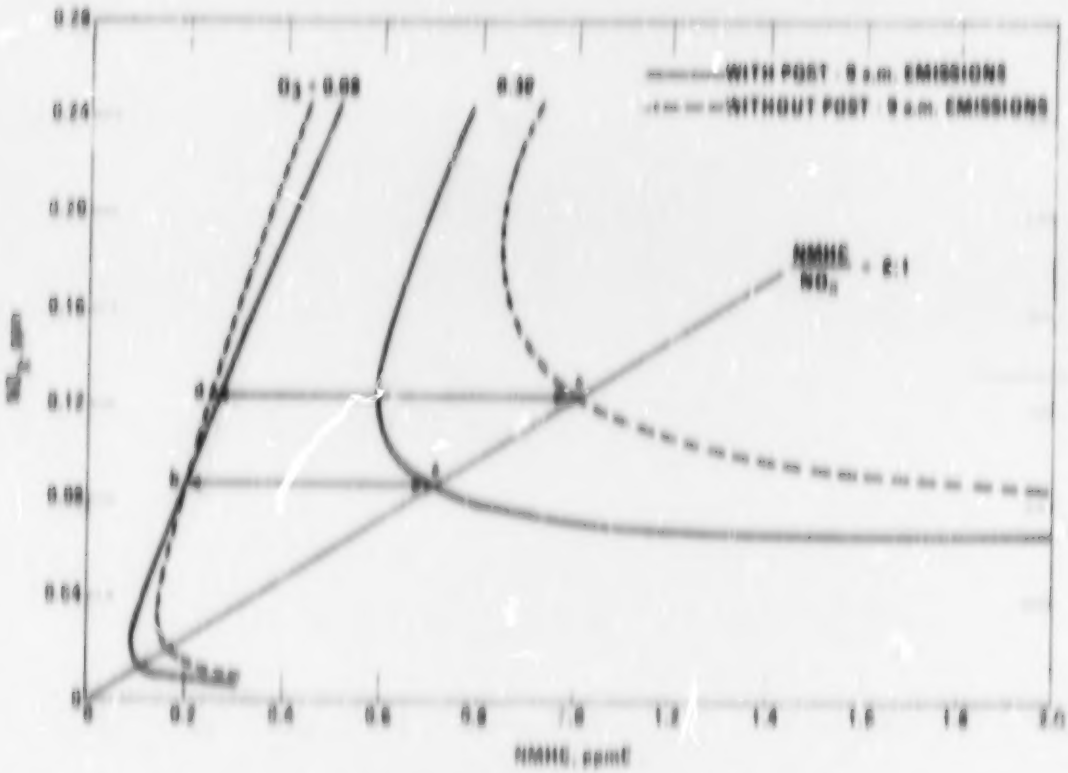

Figure 7. Comparison of isopleths with and without post-9 A.M. emissions.

and 6 are compared.

An example of the effect of including fresh emissions on the degree of NMHC control predicted to achieve the O_3 standard is diagrammed in Figure 7. With continuous emissions (solid lines), to reduce O_3 from 0.30 to 0.08 ppm at NMHC/NO_x = 8:1, NMHC should be decreased along line ab from 0.72 to 0.19 ppm. This amounts to a hydrocarbon reduction of 74%. When continuous emissions are excluded from the model (dashed lines), to meet the standards NMHC should be decreased along line cd from 1.01 to 0.25 ppm or a reduction of 75%. For this case, a difference of 1% in degree of NMHC control is predicted from the two sets of isopleths.

Additional examples of differences in control requirements predicted by the two sets of isopleths are given in Table 6. The relative change in percent hydrocarbon reduction needed to achieve the O_3 standard varies from

TABLE a. EFFECT OF POST-9 A.M. EMISSIONS ON PERCENT VOC REDUCTION NEEDED TO ACHIEVE O_3 STANDARD

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
		Without post - 9 A.M. emissions			With post-9 A.M. emissions			
$NMOC/NO_x$ (ppmC/ppm)	A (ppm)	NMOC(A) (ppmC)	NMOC(A-B) (ppmC)	Red (%)	NMOC(A) (ppmC)	NMOC(A-B) (ppmC)	Red (%)	% Change*
5:1	0.36	0.57	0.19	51	0.22	0.11	50	2
5:1	0.34	0.62	0.24	61	0.42	0.18	57	7
5:1	0.30	0.96	0.32	65	0.60	0.25	58	8
6:1	0.30	0.91	0.29	68	0.65	0.22	65	4
7:1	0.34	0.69	0.23	70	0.47	0.15	68	3
8:1	0.34	0.72	0.39	72	0.50	0.14	72	0
8:1	0.30	1.01	0.35	75	0.72	0.19	74	1
10:1	0.34	0.45	0.14	69	0.35	0.08	69	1
10:1	0.34	0.80	0.29	77	0.56	0.13	77	0
10:1	0.30	1.14	0.35	80	0.81	0.16	78	2
15:1	0.34	1.05	0.15	86	0.73	0.12	84	2
15:1	0.30	1.49	0.37	85	1.08	0.16	85	0
20:1	0.34	0.64	0.14	78	0.39	0.08	79	1

Average Change: 2%

* % Change = $\left| \frac{\text{Red}(5) - \text{Red}(8)}{\text{Red}(5)} \right| \times 100$

0 to 6%. The average relative change in predicted control requirements is only 3%, with greater reduction needed when continuous emissions are excluded from the model.

HYDROCARBON COMPOSITION

The O_3 isopleths shown in Figure 1 were generated for a hydrocarbon system comprised of 75% n-butane and 25% propylene as carbon. This composite mixture produced the best fit to smog chamber experiments of irradiated auto exhaust and NO_x mixtures. However, even in Los Angeles non-exhaust organics may comprise as much as 30-50% of the total organic emissions (6,7). Even if local emissions could be attributed solely to auto exhaust, the composition of auto exhaust may undergo change because of the impact of emission control devices (10).

Because the hydrocarbon reactivity of a particular urban area may be substantially different from the reactivity of the hydrocarbon mix employed in the smog chamber studies, it was desirable to test the sensitivity of the model predictions to changes in hydrocarbon composition. In order to gauge the maximum effect of a change in hydrocarbon composition, the composition was varied between two extremes in reactivity. In one case the n-butane content was increased to 90% and the propylene content was decreased to 10%. In the other case, a 50-50 mix of butane and propylene was used. The ratio of butane to propylene, therefore, was varied between 9:1 and 1:1, or a difference of a factor of three from the original hydrocarbon mix of 3:1. This variation in reactivity is probably considerably greater than the variations one might reasonably expect to find among urban areas. Detailed hydrocarbon analyses were made of urban air samples collected in St. Louis, Denver, Los Angeles, New Jersey, New York, and the Boston area (7, 11-13). The paraffinic content of the atmospheric samples was found to vary only from a low of 41% of the total nonmethane carbon in Los Angeles to a high of 58% in Denver and outside of Boston. The sum of the olefins and aromatic hydrocarbons in these samples ranged from 42% of the nonmethane carbon in St. Louis to 54% in Brooklyn and Los Angeles. This variation in composition is considerably less than the factor of three variation in the butane-to-propylene ratio used in this sensitivity study. The effects, therefore, of

these changes on the model predictions are expected to be significantly greater than the effect resulting from variations in hydrocarbon composition that might be found in urban areas.

The results of decreasing and increasing the reactivity of the hydrocarbon mix are discussed separately.

Decreasing Hydrocarbon Reactivity

To assess the impact of a decrease in hydrocarbon reactivity on control requirements, the simulations used to generate the isopleths of Figure 1 were repeated using a hydrocarbon mix comprised of 90% n-butane and 10% propylene (as carbon). The effect of this decrease in reactivity on the predicted O_3 levels and the degree of hydrocarbon control needed to meet the O_3 standard are described in the following two sections.

Effect on Predicted Maximum O_3 Levels

The impact of decreasing hydrocarbon reactivity on predicted levels of ozone is summarized in Table 7. The decrease in O_3 predicted for this less reactive mixture ranges from -1% at a NMHC/NO_x ratio of 100:1 to + 43% at a NMHC/NO_x ratio of 1:1. The increased O_3 concentration obtained in the high NMHC/NO_x simulation is the result of the decrease in olefinic content of the new mix. At this high ratio, hydrocarbon is present in excess. The decreased olefinic content of the less reactive mixture results in less destruction of O_3 through reaction of olefins with O_3. Ozone levels, therefore, actually increase although the overall reactivity of the system has declined. If one excludes the very high and low NMHC-to-NO_x ratios that are generally not found in urban areas, the change in O_3 yield is seen to vary from about 2 to 11% with an average difference of about 8%.

Effect on Predicted Control Requirements

The O_3 isopleths generated for the low reactivity hydrocarbon mix are shown in Figure 8. The difference between this set of isopleths and the set depicted in Figure 1 can be seen most readily by comparing the 0.08 and 0.30 ppm isopleths of Figure 9. It can be seen that the relative spacing of the isopleths is fairly consistent, but the shape of the new set of isopleths is somewhat different. There is more curvature to the new set in the high

TABLE 7. EFFECT OF HYDROCARBON REACTIVITY ON MAXIMUM 1-HOUR O_3 LEVELS

(1)	(2)	(3)	(4)	(5)	(6)
			Maximum 1-hour ozone		
$NMHC/NO_x$ (ppmC/ppm)	NMHC (ppmC)	NO_x (ppm)	75% Rollback (ppm)	90% Rollback (ppm)	% Decrease
1.0	0.10	0.10	0.421	0.412	43
2.5	0.25	0.10	0.304	0.269	34
3.33	0.33	0.15	0.196	0.148	24
5.0	0.50	0.10	0.206	0.179	18
5.0	0.25	0.05	0.126	0.117	11
6.67	1.0	0.15	0.312	0.277	11
10	1.0	0.10	0.274	0.252	8
10	2.0	0.20	0.426	0.402	6
12.5	0.25	0.02	0.098	0.098	0
20	2.0	0.10	0.320	0.312	2
50	1.0	0.02	0.154	0.152	1
100	2.0	0.02	0.142	0.144	-1

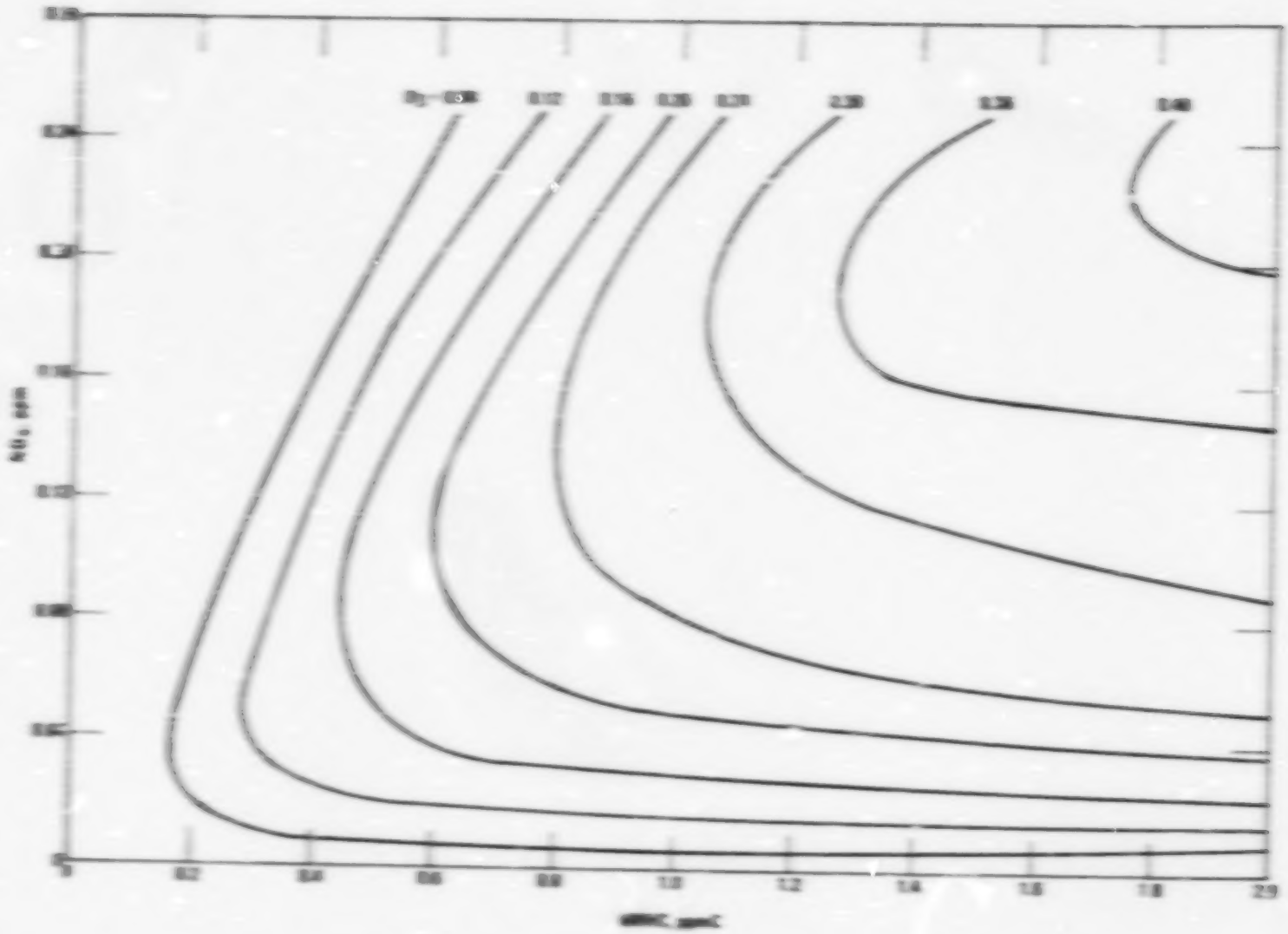

Figure 8. H_2 isopleths for 90RC mix of 30% butane and 10% propylene.

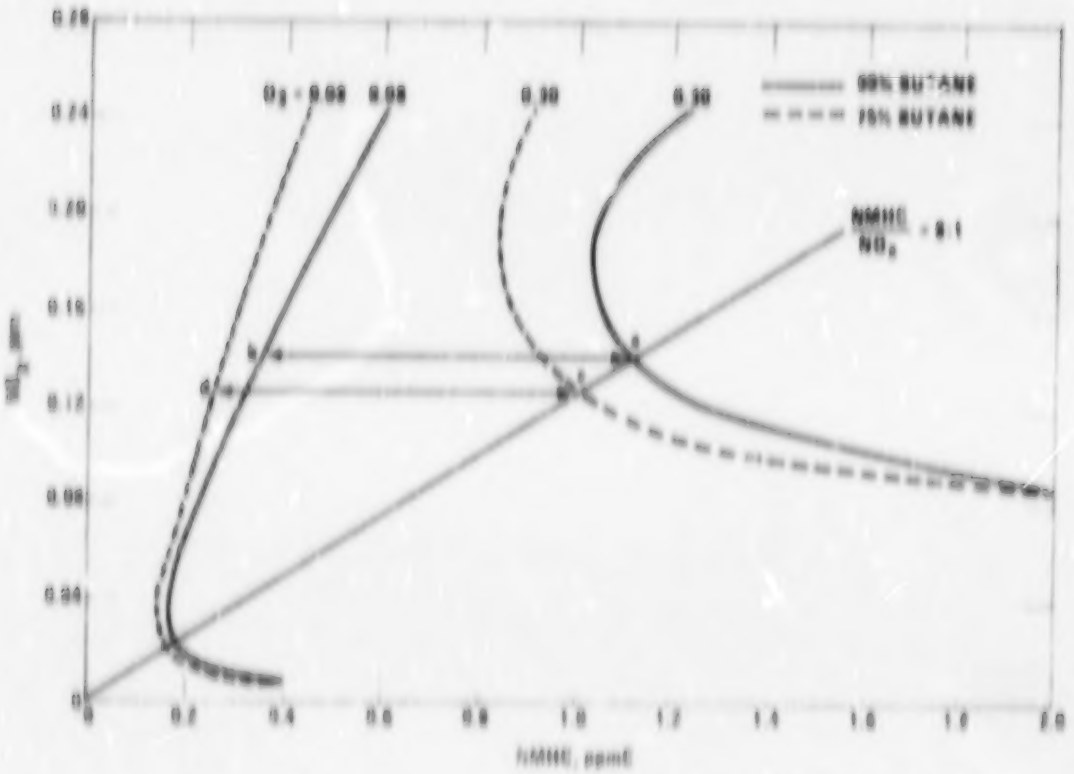

Figure 9. Comparison of isopleths for NMHC mixtures of low and medium reactivity.

NO_x region than is in the original set of isopleths (Figure 1).

Figure 9 also includes an example of the effect of decreasing hydrocarbon reactivity on the degree of control predicted to achieve the ozone standard of 0.08 ppm. At a NMHC-to-NO_x ratio of 8:1, to decrease O_3 from 0.30 to 0.08 ppm using the low reactivity set of isopleths (solid lines), NMHC should be reduced along line ab from 1.13 to 0.35 ppm. This amounts to a hydrocarbon reduction of 69%. Using the original set of isopleths (dashed lines), NMHC should be reduced along line cd from 1.01 to 0.25 ppm, or a hydrocarbon reduction of 75%. An absolute difference, therefore, of 6%, or a relative change of 8%, in degree of NMHC control is predicted from these two sets of isopleths. Other examples of the percent change in control requirements predicted from the two sets of isopleths are given in column (9) of Table 6. On

TABLE 8. EFFECT OF DECREASING HYDROCARBON REACTIVITY ON PERCENT NMHC REDUCTION NEEDED TO ACHIEVE O_3 STANDARD

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
		75% Butane-25% Propylene			90% Butane-10% Propylene			
NMHC/NO_x (ppmC/ppm)	X (ppm)	NMHC(X) (ppmC)	NMHC(.08) (ppmC)	Red (%)	NMHC(X) (ppmC)	NMHC(.08) (ppmC)	Red (%)	% Change*
5:1	0.16	0.37	0.18	51	0.45	0.24	47	8
5:1	0.20	0.50	0.21	58	0.61	0.30	51	12
5:1	0.24	0.67	0.24	64	0.83	0.39	53	15
6:1	0.30	0.91	0.29	68	1.05	0.41	61	10
7:1	0.24	0.69	0.23	70	0.81	0.29	64	9
7:1	0.30	0.96	0.26	73	1.08	0.37	66	10
8:1	0.24	0.72	0.20	72	0.84	0.27	68	6
8:1	0.30	1.01	0.25	75	1.13	0.35	69	8
8:1	0.40	1.59	0.35	78	1.77	0.53	70	10
10:1	0.16	0.45	0.14	69	0.50	0.17	66	4
10:1	0.24	0.81	0.19	77	0.82	0.25	73	5
10:1	0.30	1.14	0.23	80	1.24	0.31	75	6
15:1	0.24	1.05	0.15	86	1.11	0.21	81	6
15:1	0.30	1.48	0.22	85	1.59	0.27	83	2
20:1	0.30	1.78	0.20	89	1.87	0.25	87	2

Average Change: 7%

* % Change = $\left|\frac{\text{Col(5)} - \text{Col(8)}}{\text{Col(5)}}\right| \times 100$

the average, the hydrocarbon control predicted by the less reactive mode: is 7% less stringent than the control predicted by the original model containing the more reactive hydrocarbon mixture.

Increasing Hydrocarbon Reactivity

To assess the full impact of hydrocarbon reactivity, the simulations employed to generate the isopleths of Figure 1 were repeated using a hydrocarbon mixture that contained equal amounts of n-butane and propylene (as carbon). The effects of this increase in reactivity of the hydrocarbon mix on both the maximum O_3 levels and the predicted control requirements are discussed below.

Effect on Predicted Maximum O_3 Levels

The results of increasing hydrocarbon reactivity on peak O_3 values are summarized in Table 9. The increase in maximum O_3 levels attained with the more reactive mixture varies from +76 to -25%. The decrease in O_3 yields at the very high NMHC-to-NO_x ratios is the result of the increased olefinic content of the more reactive mix. At these high ratios, hydrocarbon is present in excess of the amount needed to drive the reaction. Since more of this excess hydrocarbon is olefinic, rather than paraffinic, in nature, more O_3 is consumed through reaction with propylene. At lower NMHC-to-NO_x ratios, where the reaction is hydrocarbon-limited, the increased reactivity of the hydrocarbon mix leads to an increase in maximum O_3 levels. If one considers only the range of NMHC/NO_x commonly found in urban areas (ratios between 5:1 and 20:1), the percent increase in O_3 is found to vary from +13 to -9%. This is considerably less variation than is found over the entire range of NMHC-to-NO_x ratios.

Effect on Predicted Control Requirements

The O_3 isopleths generated for the 50-50 mix of n-butane and propylene are shown in Figure 10. A direct comparison between these isopleths and those shown in Figure 1 is given in Figure 11. The relative spacing of these isopleths is similar, but the shape of the two sets is significantly different. The effect of this change in shape on predicted control strategy

TABLE 9. EFFECT OF INCREASING HYDROCARBON REACTIVITY ON MAXIMUM 1-HOUR O_3 LEVELS

(1)	(2)	(3)	(4)	(5)	(6)
			Maximum 1-hour ozone		
NMHC/NO_x (ppmC/ppm)	NMHC (ppmC)	NO_x (ppm)	75% Butane (ppm)	50% Butane (ppm)	% Increase
1.0	0.50	0.10	0.071	0.057	74
2.5	0.25	0.10	0.104	0.150	44
3.33	0.50	0.15	0.196	0.246	27
5.0	0.50	0.10	0.200	0.226	13
5.0	0.25	0.05	0.126	0.139	10
6.67	1.0	0.15	0.312	0.333	7
10	1.0	0.10	0.274	0.282	3
10	2.0	0.20	0.426	0.423	-1
12.5	0.25	0.02	0.098	0.102	4
20	2.0	0.10	0.318	0.290	-9
40	2.0	0.05	0.134	0.123	-8
100	2.0	0.02	0.142	0.106	-25

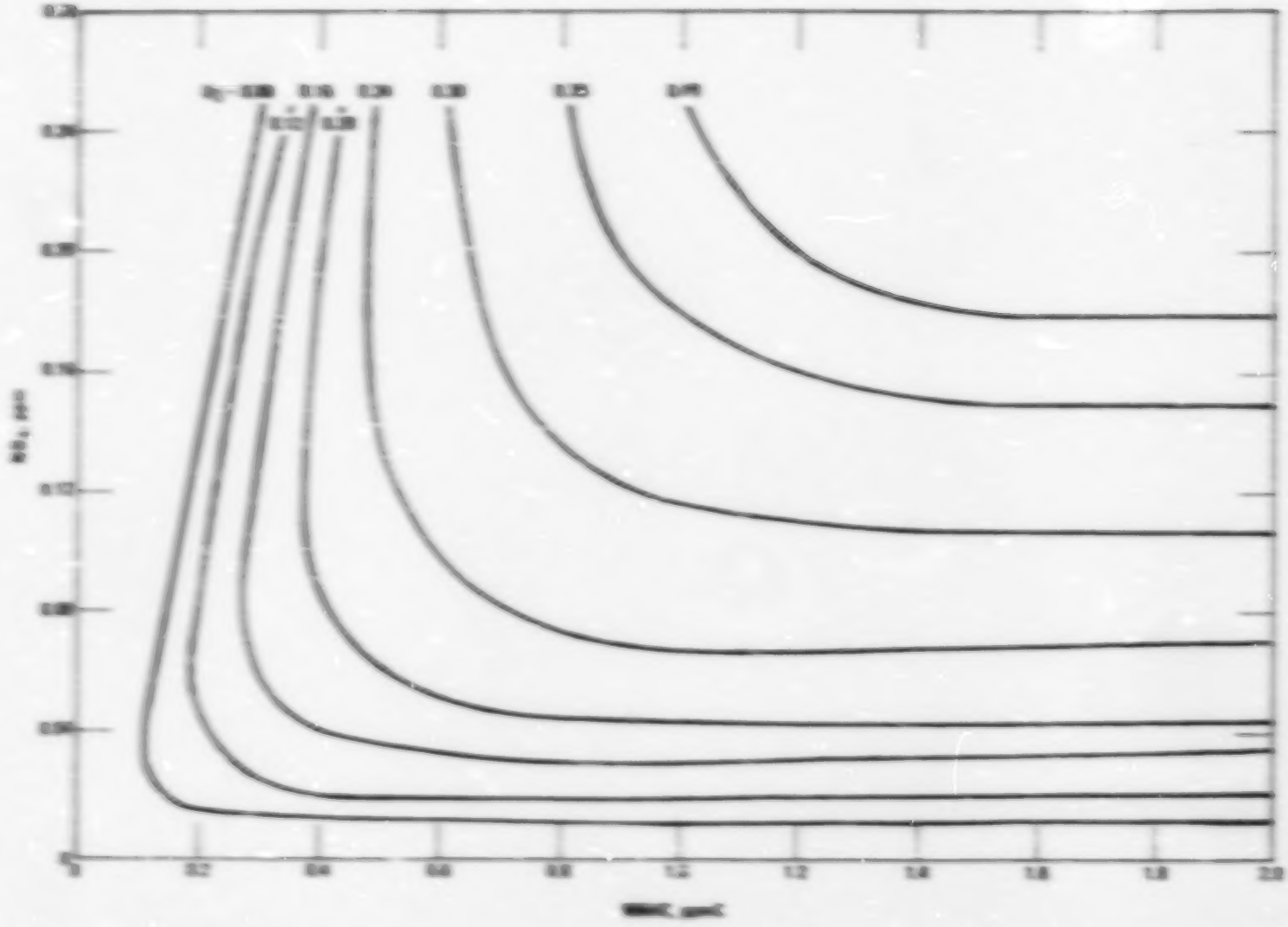

Figure 10. η_3 isopleths for WBC mix of 30% butane and 70% propylene.

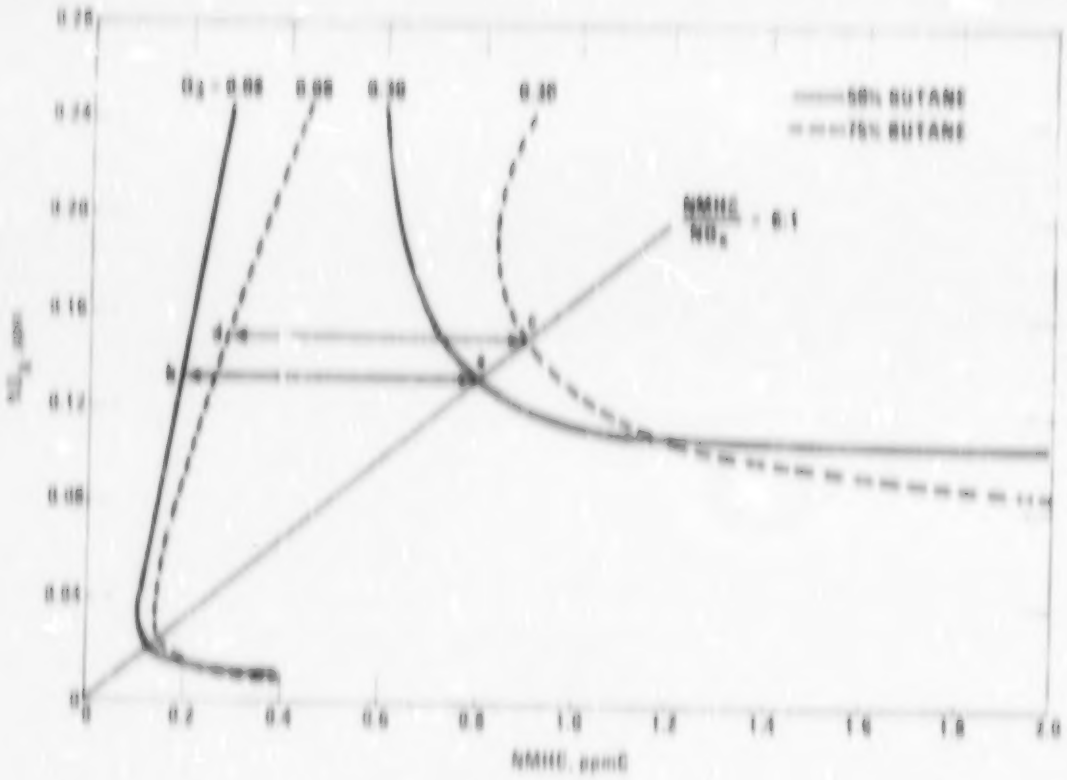

Figure 11. Comparison of isopleths for NMHC mixtures of high and medium reactivity.

is illustrated in Figure 11 for a NMHC-to-NO_x ratio of 8:1 and a peak O_3 level of 0.30 ppm. For the highly reactive system (solid lines), the model indicates that NMHC should be decreased along line ab from 0.80 to 0.19 ppm, or a hydrocarbon reduction of 76%. Using the original set of isopleths (dashed lines) for the less reactive mix, NMHC should be reduced along line cd from 0.91 to 0.20 ppm, or a hydrocarbon control of 78%. The new set of isopleths, therefore, indicates the need for an 8% greater reduction of hydrocarbons, or, a relative increase in control requirements of 12%. Additional examples of the predicted differences in hydrocarbon reduction derived from the two sets of isopleths are given in Table 10. The average relative change in predicted hydrocarbon control is 8%, with greater control required for the hydrocarbon mix of high reactivity.

TABLE 10. EFFECT OF INCREASING HYDROCARBON REACTIVITY ON PERCENT NMHC REDUCTION NEEDED TO ACHIEVE O_3 STANDARD

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
		75% Butane-25% Propylene			50% Butane-50% Propylene			
NMHC/NO_x (ppmC/ppm)	X (ppm)	NMHC(X) (ppmC)	NMHC(.08) (ppmC)	Red (%)	NMHC(X) (ppmC)	NMHC(.08) (ppmC)	Red (%)	% Change*
5:1	0.20	0.50	0.21	58	0.40	0.14	65	12
5:1	0.24	0.62	0.24	61	0.55	0.17	69	13
6:1	0.30	0.91	0.29	68	0.80	0.19	76	12
6:1	0.40	1.42	0.42	70	1.20	0.25	79	13
7:1	0.24	0.69	0.21	70	0.64	0.15	77	10
7:1	0.30	0.96	0.24	75	0.87	0.18	79	6
8:1	0.24	0.72	0.20	72	0.68	0.14	79	10
8:1	0.30	1.01	0.25	75	0.94	0.17	82	9
8:1	0.40	1.58	0.25	78	1.47	0.23	84	8
10:1	0.16	0.45	0.14	69	0.40	0.11	72	4
10:1	0.24	0.81	0.19	77	0.76	0.13	83	8
10:1	0.30	1.14	0.23	80	1.13	0.16	86	7
15:1	0.24	1.05	0.15	86	1.02	0.12	88	2
15:1	0.30	1.48	0.22	85	1.42	0.14	90	6
20:1	0.24	1.37	0.16	87	1.40	0.12	91	5

Average Change: 6%

* $\%\ \text{Change} = \left| \frac{\text{Col (5)} - \text{Col (8)}}{\text{Col (5)}} \right| \times 100$

Summary of Reactivity Effects

The sensitivity studies of hydrocarbon reactivity presented above indicate that a factor of three variation in the butane-to-propylene ratio results in an average change in predicted hydrocarbon control requirements of only 7-8%. The variation in hydrocarbon reactivity used in these studies is suspected to be considerably greater than the variation in reactivity that might be found in urban areas. It is reasonable to conclude, therefore, that predicted control requirements are relatively insensitive to expected variations in hydrocarbon reactivity.

In addition to investigating the effect of hydrocarbon reactivity, the sensitivity of the model to changes in the initial NO_2-to-NO_x ratio was also investigated. The isopleths of Figure 1 were generated for an initial NO_x mix comprised of 25% NO_2 and 75% NO. Almost all oxides of nitrogen are emitted in the form of NO. For example, more than 90% of the NO_x emissions from power plants are in the form of NO (14). The 6-9 A.M. ratio of NO_2-to-NO_x of 1:4 used in the simulations was chosen to reflect the presence of aged pollutants in an urban area. These aged pollutants may result from carry-over from the preceding day or transport from upwind locations. It is reasonable to expect that the 6-9 A.M. ratio of NO_2-to-NO_x may vary among urban areas. To assess the effect of such variations on the predictions of the model, two series of simulations were carried out. In one series, the initial NO_2 concentration was taken to be 10% of the initial NO_x. In the other series of runs, NO_2 was taken to be 50% of the initial NO_x concentration. Ten pairs of simulations were carried out for NMHC-to-NO_x ratios that ranged from 5:1 to 50:1. It was found that the time to the O_3 peak depended on the initial NO_2-to-NO_x ratio as one would expect. O_3 reached a maximum earlier in the day in those simulations where NO_2 was taken to be 50% of the NO_x. The absolute peak O_3 levels, however, were largely insensitive to the initial NO_2 concentration. The difference in maximum O_3 concentration for each pair of runs was 3% or less. For all ten pairs of runs where NO_2 was 10% and 50% of the initial NO_x, the average change in peak ozone concentration was 1%. Since variations in the NO_2-to-NO_x ratio had negligible effect on the absolute O_3 levels, it can be concluded that control requirements also are not affected by this parameter.

SECTION 5

DISCUSSION

The preceding section presented the results of sensitivity studies that were conducted to assess the impact of various parameters on the predictions of the photochemical model. Ozone isopleths were constructed for each of the five test cases considered. These sets of isopleths were found to differ somewhat from the original isopleths of Figure 1 in either shape or relative spacing or both. The absolute positioning of the O_3 isopleths is of little concern since the isopleths will be applied in a relative sense. The isopleths will be used only to assess the sensitivity of peak O_3 concentrations to changes in 6-9 A.M. levels of NMHC and NO_x. Our concern, therefore, is only with the differences in shape and spacing of the various isopleths and how these differences affect the predicted benefit in ambient O_3 levels to be gained from various control strategies. To this end, four hypothetical control strategies have been selected. The results anticipated by applying these strategies to each of the six sets of isopleths will be compared.

For purposes of illustration, assume a maximum O_3 concentration of 0.24 ppm is observed in a given urban area with a median NMHC-to-NO_x ratio of 8:1. The four control strategies under consideration are:

Strategy I: Determine the percent reduction in 6-9 A.M. NMHC needed to obtain the 0.08 ppm O_3 standard assuming no change in ambient NO_x levels is anticipated.

Strategy II: Determine the percent reduction in 6-9 A.M. NMHC needed to obtain the 0.08 ppm O_3 standard if a 25% reduction in ambient NO_x levels is anticipated.

Strategy III: Determine the reduction in O_3 levels anticipated if NMHC emissions are reduced by 50% while NO_x emissions remain the same.

Strategy IV: Determine the reduction in O_3 levels anticipated if both NMHC and NO_x emissions are reduced by 50%.

These four control strategies were applied to each of the six sets of isopleths (Figures 1,2,4,6,8, and 10). The results are summarized in Table II. Columns (1) and (2) describe the isopleths used to calculate the effects of the various control strategies. Columns (3) and (4) list the percent hydrocarbon reduction needed to achieve Strategies I and II, respectively. Columns (5) and (6) give the anticipated O_3 level to be achieved when Strategies III and IV are applied, respectively.

As an example of how the calculations were made, consider the four strategies involving the use of Figure 1. An O_3 level of 0.24 ppm at a NMHC-to-NO_x ratio of 8:1 corresponds to NMHC = 0.72 ppm and NO_x = 0.092 ppm. Strategy I is implemented by reducing NMHC at constant NO_x until it intercepts the 0.08 ppm O_3 isopleth. This occurs at a NMHC concentration of 0.20 ppm or a reduction in NMHC levels of 72%.

Strategy II calls for a 25% reduction in NO_x levels from NO_x = 0.092 to NO_x = 0.069 ppm. Strategy II is applied by reducing NMHC at this lower NO_x level of 0.069 ppm until it intercepts the 0.08 ppm O_3 isopleth. This occurs at a NMHC concentration of 0.17 ppm, or a reduction in NMHC levels of 76%.

To apply Strategy III, a 50% reduction in nonmethane hydrocarbon corresponds to 0.72/2 = 0.36 ppm. This NMHC value and the original NO_x level of 0.092 ppm intercept the 0.16 ppm O_3 isopleth.

To apply Strategy IV, NO_x is reduced by 50% from 0.092 to 0.046 ppm. This NO_x concentration and a NMHC concentration of 0.36 ppm define a point located between the 0.12 and 0.16 ppm O_3 isopleths. Extrapolating, it appears this point corresponds to an O_3 concentration of about 0.15 ppm.

Similarly, the calculations were made with the other five sets of isopleths. For all four control strategies, the agreement is good. For control Strategy I, the absolute percent reduction in NMHC levels varies from 68 to 78%. If the isopleths of Figure 1, therefore, were selected for use in planning control strategies, the control of hydrocarbon emissions derived from Figure 1 might be too stringent by 4% or too lenient by 7%, based on these sensitivity studies. For Strategy II, the percent reduction in NMHC levels needed to achieve the O_3 standard varies from 74 to 81%. If the isopleths of Figure 1 are used in planning control requirements, the control of NMHC might be too stringent by

TABLE II. COMPARISON OF SELECTED CONTROL STRATEGIES APPLIED TO SIX SETS OF O_3 ISOPLETHS

(1)	(2)	(3)	(4)	(5)	(6)
		Strategy			
	O_3 Isopleths	I VOC Red (const. NO_x) %	II VOC Red (reduced NO_x) %	III O_3 Max (const. NO_x) ppm	IV O_3 Max (reduced NO_x) ppm
Fig.	Description				
1	Standard	72	76	0.20	~0.15
2	Decreased light intensity	71	76	0.16	~0.15
4	Increased dilution rate	68	76	~0.14	~0.14
6	Post-8 A.M. emissions	72	76	~0.17	0.16
8	Decreased reactivity	68	74	~0.*1	~0.14
10	Increased reactivity	79	81	~0.19	0.16

25 or too lenient by 55. Likewise, for Strategy III, the anticipated O_3 reduction to 0.16 ppm might be as great at 0.1s ppm or as little as 0.18 ppm, a difference of 0.02 ppm or approximately 12%. For Strategy IV, there is a difference of only 0.01 ppm or a relative change of 7% in O_3 levels predicted by using Figure 1 rather than one of the other sets of isopleths.

These results indicate that the selection of initial conditions has little effect on the predictions of the model in relation to the expected benefit to be derived from various control strategy options. The six sets of isopleths give essentially identical results when applied in a relative sense. Although the isopleths of Figure 1 were derived for conditions that perhaps would be found more often in Los Angeles than in other areas of the country, the isopleths should still be applicable to other localities.

The studies presented here only test the sensitivity of the model to changes in initial conditions. How well the results relate to the real-world situation is, of course, subject to speculation. The proposed method was developed through analysis of smog chamber data, with the intent of accurately representing the chemistry occurring in static smog systems. It is a compromise between the existing Appendix J method, which ignores the role of NO_x in ozone formation, and the urban diffusion models under development that have the capacity to treat meteorology as well as chemistry. Viewed in this respect, the advantages and limitations of the proposed method are apparent. The limitations associated with the method are such that the O_3 isopleths of Figure 1 should not be interpreted in an absolute sense. The results of the sensitivity studies, however, indicate that the isopleths appear valid when viewed in a relative sense.

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APPENDIX

REACTION MECHANISM USED TO GENERATE O_3 ISOPLETHS

Number	Reaction	Rate Constant[c]
1	$NO_2 + h\nu \rightarrow NO + O(^3P)$	k_{very}
2	$O(^3P) + O_2 + M \rightarrow O_3 + M$	2.0×10^{-5} ppm^{-2}min^{-1}
3	$O_3 + NO \rightarrow NO_2 + O_2$	25.0
4	$NO_2 + O_3 \rightarrow NO_3 + O_2$	0.04
5	$NO_2 + O(^3P) \rightarrow NO + O_2$	1.5×10^4
6	$NO_3 + NO \rightarrow 2NO_2$	1.5×10^4
7	$NO_2 + NO_3 \rightarrow N_2O_5$	5.6×10^3
8	$N_2O_5 \rightarrow NO_2 + NO_3$	22.0 min^{-1}
9	$N_2O_5 \rightarrow 2HNO_3$	2.5×10^{-6}
10	$NO + NO_2 + H_2O \rightarrow 2HONO$	1.0×10^{-9} ppm^{-2}min^{-1}
11	$2HONO \rightarrow NO + NO_2 + H_2O$	1.0×10^{-3}
12	$HONO + h\nu \rightarrow OH + NO$	k_{very}
13	$OH + NO_2 \xrightarrow{M} HNO_3$	8.0×10^3
14	$OH + CO \xrightarrow{M} HOCO$	3.0×10^3
15	$HO_2 + NO \rightarrow NO_2 + OH$	1.2×10^4
16	$HO_2 + HO_2 \rightarrow HOOH + O_2$	5.4×10^3
17	$HOOH + h\nu \rightarrow 2OH$	k_{very}
18	$O_3 + h\nu \rightarrow O(^1D)$	k_{very}
19	$O_3 + h\nu \rightarrow O(^3P)$	k_{very}
20	$O(^1D) + M \rightarrow O(^3P) + M$	8.7×10^4
21	$O(^1D) + H_2O \rightarrow 2OH$	5.1×10^5
22	$OH + O_3 \rightarrow HO_2 + O_2$	84.0

Number	Reaction	Rate Constant[a]
23	$O_3 + HO_2 \rightarrow OH + 2O_2$	2.4
24	PROP + OH → ADD	2.5×10^4
25	ADD + NO → R + NO_2	1.0×10^3
26	ADD + ADD → 2R	1.2×10^4
27	ADD + MeO_2 → R + MeO	1.0×10^3
28	ADD + C_2O_2 → R + C_2O	1.0×10^3
29	ADD + C_3O_2 → R + C_3O	1.0×10^3
30	ADD + C_4O_2 → R + C_4O	1.0×10^3
31	ADD + ScO_2 → R + ScO	1.0×10^3
32	R → HCHO + ALD2 + HO_2	1.0×10^5 min^{-1}
33	PROP + O_3 → OH + HO_2 + ALD2	8.0×10^{-3}
34	PROP + O_3 → OH + C_2O_3 + HCHO	8.0×10^{-3}
35	BUT + OH → ScO_2	1.8×10^3
36	BUT + OH → C_4O_2	1.8×10^3
37	NO + C_4O_2 → NO_2 + C_4O	1.8×10^3
38	NO + ScO_2 → NO_2 + ScO	1.8×10^3
39	NO + C_3O_2 → NO_2 + C_3O	1.8×10^3
40	NO + C_2O_2 → NO_2 + C_2O	1.8×10^3
41	NO + MeO_2 → NO_2 + MeO	1.8×10^3
42	C_4O → HCHO + C_3O_2	7.5×10^4 min^{-1}
43	ScO → ALD2 + C_2O_2	1.0×10^5 min^{-1}
44	C_3O → HCHO + C_2O_2	8.0×10^3 min^{-1}
45	C_2O → HCHO + MeO_2	4.0×10^3 min^{-1}
46	C_4O + O_2 → ALD4 + HO_2	0.7
47	ScO + O_2 → HCO + HO_2	1.4

Number	Reaction	Rate Constant[a]
48	$C_3O + O_2 \rightarrow ALD3 + HO_2$	0.5
49	$C_2O + O_2 \rightarrow ALD2 + HO_2$	0.4
50	$MeO + O_2 \rightarrow HCHO + HO_2$	0.4
51	$HCHO + h\nu \rightarrow$ Stable Products	k_{very}
52	$HCHO + h\nu \rightarrow 2HO_2$	k_{very}
53	$HCHO + OH \rightarrow HO_2$	1.5×10^4
54	$ALD2 + h\nu \rightarrow$ Stable Products	k_{very}
55	$ALD2 + h\nu \rightarrow MeO_2 + HO_2$	k_{very}
56	$ALD2 + OH \rightarrow C_2O_3$	1.5×10^4
57	$ALD3 + h\nu \rightarrow$ Stable Products	6.0×10^{-5} min^{-1}
58	$ALD3 + h\nu \rightarrow C_2O_2 + HO_2$	2.5×10^{-3} min^{-1}
59	$ALD3 + OH \rightarrow C_3O_3$	4.5×10^4
60	$ALD4 + h\nu \rightarrow$ Stable Products	6.0×10^{-5} min^{-1}
61	$ALD4 + h\nu \rightarrow C_3O_2 + HO_2$	1.9×10^{-3} min^{-1}
62	$ALD4 + OH \rightarrow C_4O_3$	4.5×10^4
63	$C_4O_3 + NO \rightarrow C_3O_2 + NO_2$	8.0×10^2
64	$C_3O_3 + NO \rightarrow C_2O_2 + NO_2$	8.0×10^2
65	$C_2O_3 + NO \rightarrow MeO_2 + NO_2$	8.0×10^2
66	$C_4O_3 + NO_2 \rightarrow$ PAN	1.0×10^2
67	$C_3O_3 + NO_2 \rightarrow$ PAN	1.0×10^2
68	$C_2O_3 + NO_2 \rightarrow$ PAN	1.0×10^2
69	$C_4O_2 + HO_2 \rightarrow$ Stable Products	4.0×10^3
70	$C_3O_2 + HO_2 \rightarrow$ Stable Products	4.0×10^3
71	$MeO_2 + HO_2 \rightarrow$ Stable Products	4.0×10^3

Number	Reaction	Rate Constant*
73	$C_2O_3 + HO_2 \rightarrow$ Stable Products	4.0×10^3
74	$MeO_2 + HO_2 \rightarrow$ Stable Products	4.0×10^3
75	$C_4O_3 + HO_2 \rightarrow$ Stable Products	4.0×10^3
76	$C_5O_3 + HO_2 \rightarrow$ Stable Products	4.0×10^3
77	$C_6O_3 + HO_2 \rightarrow$ Stable Products	4.0×10^3

* Units of $ppm^{-1}min^{-1}$ unless otherwise indicated

Symbol	Definition
k_{very}	Diurnal 1-hour average photolytic rate constant
PROP	C_3H_6
BUT	$n\text{-}C_4H_{10}$
ARD	$CH_3CH(OH)CH_2CHO$
6	$CH_3CH(OH)CH_2O$
MeO_2	CH_3O_2
C_2O_2	$CH_3CH_2O_2$
C_3O_2	$CH_3CH_2CH_2O_2$
C_4O_2	$CH_3CH_2CH_2CH_2O_2$
$SecO_2$	$CH_3CH(O_2)CH_2CH_3$
ALD1	CH_3CHO
ALD2	CH_3CH_2CHO
ALD4	$CH_3CH_2CH_2CHO$
C_2O_3	CH_3CO_3
C_3O_3	$CH_3CH_2CO_3$
C_4O_3	$CH_3CH_2CH_2CO_3$